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Published in:
Macromolecules

DOI:
10.1021/ma9508358

Communications to the Editor

Oriented Thin Film Formation by Surface Graft Polymerization of γ-Methyl L-Glutamate *N*-Carboxyanhydride in the Melt

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Received June 14, 1995

This paper describes a new and versatile method to produce grafted layers of poly(γ-methyl L-glutamate) (PMLG) on silicon wafers by the ring-opening polymerization of γ-methyl L-glutamate *N*-carboxyanhydride (MLG-NCA). Compared with the polymerizations in solution,[1,2] this approach provides grafted synthetic polypeptide layers very easily and reproducibly.

Leuchs[3] already polymerized NCAs using water as an initiator in 1906. Blout and Karlson[4] demonstrated for the first time the polymerization of γ-benzyl L-glutamate NCA, initiated by trialkylamines, producing α-helical polypeptides with a high molecular weight. Since then, polyglutamates have been the subject of numerous studies.[5]

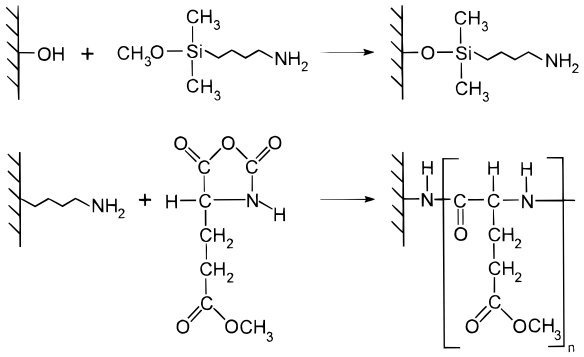
To obtain grafted polymeric layers, immobilized primary amines can be used. These amines initiate the ring-opening polymerization of NCAs according to the amine mechanism[6] leading to surface-grafted polymer chains. This method has been used by many researchers to graft polypeptides in rather high yields onto Aerosil A200V,[1,7] carbon black,[8] and other polymers bearing free primary amine groups.[9−11]

The grafting of polyglutamates from flat substrates like glass slides or silicon wafers is much more difficult. Compared with Aerosil, flat substrates have much smaller specific surface areas, resulting in much smaller numbers of immobilized initiator groups, inducing a high sensitivity to impurities.

The properties of these very thin grafted layers can be tuned very easily by functionalization of the glutamic acid monomer unit. Numerous LB studies indicated the applicability of polyglutamates in chemical sensors[12] and membranes for transport of ions,[13,14] electrons,[15,16] and other small molecules[17,18] to mimic biological functions. The optical activity of many polyglutamates[19] can lead to applications in the fields of waveguides,[20] data storage,[21,22] and nonlinear optics.[23,24] Recently, Whitesell and Chang[25] published the polymerization of alanine NCAs initiated by amine-functionalized gold substrates, producing highly ordered polymeric films with α-helices oriented nearly perpendicular to the surface.

In the present study, ring-opening polymerization of γ-methyl L-glutamate *N*-carboxyanhydride was investigated. MLG-NCA was synthesized according to the procedure published by Dorman et al.[26] The silicon wafers (Topsil Semiconductor Materials A/S, Frederikssund, Denmark, both sides polished) were cleaned prior to the silanization step. After ultrasonic cleaning in ethanol and dichloromethane, the wafers were treated with a hot $NH_3/H_2O_2/H_2O$ (1:1:5 v/v/v) mixture for 25 min. After extensive rinsing with Milli-Q water, the wafers were sonicated in a mixture of concentrated HCl/H_2O (1:6 v/v) for 25 min and rinsed again with large amounts of water. After rinsing with methanol, methanol/toluene (1:1 v/v), and toluene, the cleaned wafers were immediately silanized with (4-aminobutyl)dimethylmethoxysilane (ABMS) according to the method of Haller.[27] After dissolving the monomer in ultradry THF (0.1 mol/L), this solution was spin-coated onto the silanized wafers using different spinning rates. After evaporation of the solvent during spinning, the samples were transferred to a heating oven.

Scheme 1



Polymerizations (see Scheme 1) were performed in the melt by heating the samples to 105 °C, just above the melting temperature of the NCA monomer (98−99 °C).[26] Usually, reaction times of 30 min were enough for complete monomer conversion. At these temperatures, a substantial amount of nongrafted polymeric material is also formed. This is caused by thermal initiation.[28] This nongrafted material could easily be removed by washing the samples with a chloroform/dichloroacetic acid mixture (80:20 v/v) during one night.

Characterization of the obtained thin layers was performed by XPS analysis (X-Probe 300 of Surface Science Instruments, using monochromated Al Kα radiation with an energy of 1486.6 eV; each sample was measured with an experimental resolution of 1.8 eV; take-off angle, 45°) and FT-IR transmission spectroscopy (Mattson Galaxy 6020; 256 scans; resolution, 4 cm^{-1}).

XPS measurements were done after each step of the synthetic procedure. The presence of the aminosilane coupling layer can be seen by comparing the XPS spectra shown in Figure 1a and b. In particular, the N(1s) peak at 400 eV clearly indicates the existence of the coupling layer.

Figure 1c shows the XPS spectrum of the PMLG layer. The disappearances of the Si(2s) peak at 150 eV and the Si($2p_3$) peak at 99 eV are due to the thickness of the grafted layer of about 20 nm, as calculated from combined FT-IR and thickness measurements (Dektak 3030 ST). The limiting depth of XPS analysis is about 5−10 nm. The enlarged peaks of C(1s) at 285 eV and N(1s) at 400 eV also prove that the polymeric layer has been formed.

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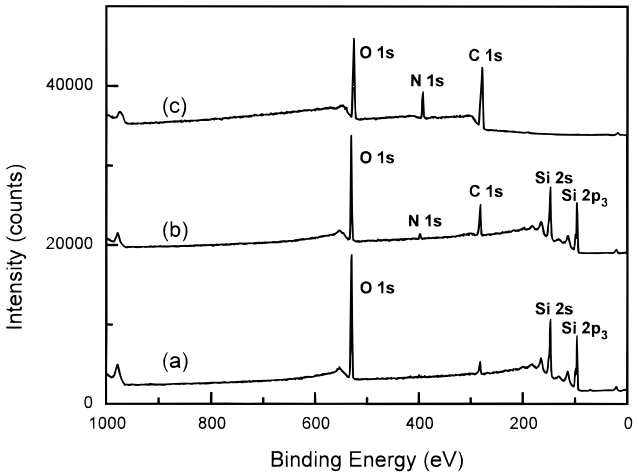

Figure 1. XPS spectra of (a) clean wafer, (b) silanized wafer, and (c) grafted PMLG layer.

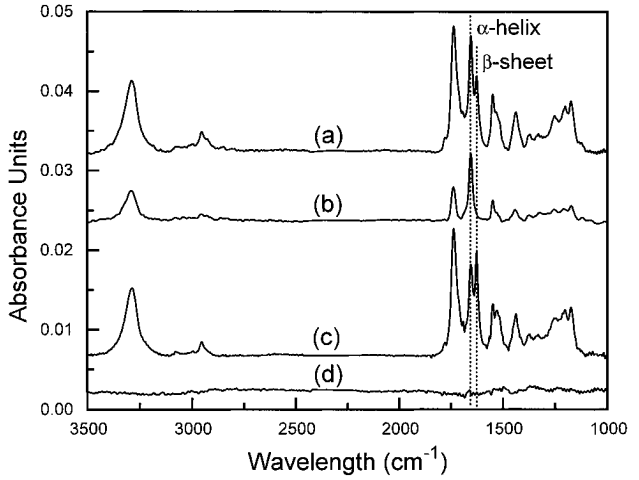

Figure 2. FT-IR transmission spectra of polymerization of MLG-NCA with initiator (a) before and (b) after washing and without initiator (c) before and (d) after washing.

The apparent decrease of the O(1s) peak at 530 eV is a result of the combination of the vanishing oxygen signal of the silicon oxide layer and the increasing oxygen signal of the polymer layer.

Figure 2 shows the FT-IR transmission spectra before (a) and after (b) the washing procedure. The ester side chain carbonyl is believed to have a random orientation,[29] so this absorption band can be taken as a measure for the amount of polymer on the substrate. It is clear that about 20% of the total amount of polymerized material is actually grafted. These grafted polymer chains take on the pure α-helical conformation, as can be concluded from the absorptions of the amide I (1653 cm^{-1}) and amide II (1550 cm^{-1}).[30] The ungrafted thermally initiated fraction consisted of α-helices and a substantial amount of polymer in the β-sheet conformation, as was deduced from the positions of the absorptions of the amide I (1632 cm^{-1}) and amide II (1529 cm^{-1}).

The effect of the primary amine initiator can easily be seen by comparing the spectra in Figure 2. Without the amine initiator, the amount of β-sheet formation is much larger (c), and after the washing procedure, the formed polymeric material is totally removed from the substrate in about 15 min (d). When the surface of the substrate is covered with amine groups, however, less β-sheet is formed (a), and after washing, only α-helical material is left on the substrate (b).

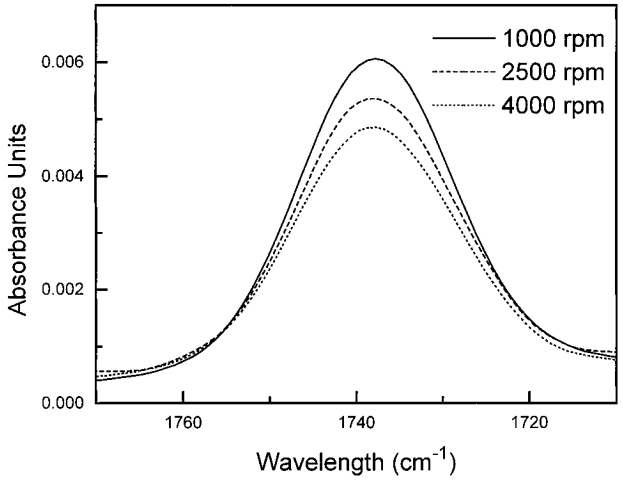

Figure 3. FT-IR transmission spectra of grafted PMLG layers, using different spinning rates during spin-coating.

The orientation of the helices with respect to the plane of the substrate can be deduced from comparison of the spectra in Figure 2 with spectra of Langmuir−Blodgett films of polyglutamates, as published in the literature.[29] The ratio of the amide I and amide II bands, which have almost mutually perpendicular transition dipole moments, can give a good indication of the orientation of the helical chains. For the LB films with the helices parallel to the substrate, this results in a very high amide I absorption and a very small amide II absorption. The much lower amide I absorption and the much higher amide II absorption in our case suggest a more perpendicular orientation of the helices relative to the substrate.

The total amount of grafted material can be controlled to some extent by varying the spinning rates during spin-coating. Figure 3 shows the FT-IR transmission spectra of the ester side chain C═O absorption of the grafted fractions obtained after spin-coating at 1000, 2500, and 4000 rpm. Higher spinning rates result in lower intensities of the C═O absorption, meaning smaller amounts of grafted polymer.

Surface grafting of synthetic polypeptides onto flat substrates can easily be carried out by applying a thin coating of pure monomers onto silicon wafers that have been pretreated with a primary amine function containing silanization agent, just by spin-coating a solution and subsequently heating the samples above the melting points of the monomers. The grafted layers consist of pure α-helical polypeptides. These helices stretch away from the surface, depending on the grafting density and side chain interactions. Various layer characterization techniques, like ellipsometry and X-ray total reflectivity measurements, and more FT-IR dichroic measurements for orientation studies will be part of further research.

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MA9508358